

# The effects of polydispersity and metastability on crystal growth kinetics

J. J. Williamson\* and R. M. L. Evans  
*Soft Matter Group, School of Physics and Astronomy,  
 University of Leeds, Leeds LS2 9JT United Kingdom*  
 (Dated: August 21, 2012)

We investigate the effect of metastable gas-liquid (G-L) separation on crystal growth in a system of either monodisperse or slightly size-polydisperse square well particles, using a simulation setup that allows us to focus on the growth of a *single* crystal. Our system parameters are such that, inside the metastable G-L binodal, a layer of the gas phase ‘coats’ the crystal as it grows, consistent with experiment and theoretical free energy considerations. Crucially, the effect of this metastable G-L separation on the crystal growth rate depends qualitatively on whether the system is polydisperse. We measure reduced polydispersity in the crystal relative to the fluid, and propose that the required fractionation is dynamically facilitated by the gas layer. Our results show that polydispersity and metastability, both ubiquitous in soft matter, must be considered in tandem if their dynamical effects are to be understood.

PACS numbers: 82.70.-y, 64.75.Gh, 64.60.-i

## I. INTRODUCTION

Substances in the category of ‘soft condensed matter’ (colloidal suspensions, polymers, proteins etc.), as well as having widespread industrial and medical importance, are interesting in their own right because they exhibit physics analogous to that of simpler molecular or atomic systems, but on much longer time- and length-scales [1]. The analogy stems from the importance of thermal fluctuations in the microscopic dynamics of the constituents, which means that the same thermodynamic and statistical mechanical approaches can be applied in both cases [2]. Nonetheless, the study and exploitation of soft matter presents a number of challenges, two of which are the focus of the present work.

Firstly, a collection of mesoscopic particles which are nominally the same will almost certainly be *polydisperse*, i.e. will exhibit a distribution in properties such as size, charge, shape or chemical makeup. This is in contrast to e.g. a molecular fluid of pure water in which, in a strict sense, every molecule is identical. Efforts by various workers to describe the thermodynamics of polydisperse systems [3–10] have resulted so far in a reasonably firm understanding of the effects of a mild degree of polydispersity on the *equilibrium* phase diagrams of hard spheres and related systems. Beyond this, polydispersity remains a pervasive but poorly understood complicating factor in soft matter physics – in particular, its effects on phase ordering kinetics as actually enacted in real systems are unclear [11–16], and quantitative theoretical work thereon is almost non-existent [17, 18].

Secondly, and in common with simpler systems, soft matter’s path towards equilibrium may be influenced by the presence of *metastable* states. These are the result of local minima in the free energy landscape which, although they do not fully minimise the free energy of the

system (and therefore do not appear in the equilibrium phase diagram), may be encountered as an intermediate stage. They may be long-lived, especially if the system must overcome some free energy barrier in order to reach its global minimum. A prime example is the metastable gas-liquid (G-L) separation of attractive particles, which may subsequently progress to equilibrium crystal-fluid coexistence [16]. The influence of metastability on phase ordering is a problem of general importance, with particular application in e.g. colloid-polymer mixtures and protein crystallisation [19–22].

In this paper, we perform simulations which focus on crystal *growth* (as distinct from nucleation) in a model colloidal system exhibiting the metastable G-L coexistence described above. By varying the interaction strength and size polydispersity, we study the effects of metastability and polydispersity on the crystal growth dynamics. For our parameters, we find that the metastable G-L separation results in a gaseous layer coating the growing crystal, an observation which we relate to theoretical free energy curves and existing experimental work. When polydispersity is present, this layer can act to speed up crystal growth, in contrast to the monodisperse case in which crystal growth is *slowed* by the presence of the gas layer. Interpreted as a dynamical phenomenon, this suggests that fractionation at the crystal interface, relying on self diffusion, is facilitated by the gas layer. Our results shed light on the influence of polydispersity and metastability on the crystal growth process, demonstrating the complex way in which these factors can interact.

The structure of the paper is as follows. In Section II we describe the simulation apparatus and the parameters used, with reference to the equilibrium phase diagram of our system. In Section III we outline two pertinent theoretical aspects of the work, viz. the free energy landscape of the system, and the diffusive growth of split interfaces of the kind which our simulations exhibit. In Section IV we present the simulation results and discuss the effects

---

\* pyjjw@leeds.ac.uk

of metastability, polydispersity, and the two combined on the crystal growth process. Finally, in Section V, we outline and briefly test a possible explanation for the complex interaction between metastability and polydispersity, before concluding and motivating future work in Section VI.

## II. SIMULATION

### A. Kinetic Monte Carlo algorithm

The simulation is built on a Kinetic Monte Carlo (KMC) algorithm, in which the available trial moves are limited to small stochastic ‘hops’, representing the inertia-free Brownian motion of colloidal particles dispersed in a solvent. Therefore, in contrast to equilibrium MC methods, KMC is suitable for studying the dynamics of phase transitions since unphysical moves such as cluster rearrangements, particle resizing etc., which are helpful in speeding up equilibration, are not used. In common with comparable Molecular or Brownian Dynamics methods, hydrodynamic interactions are neglected. Further details of our implementation are available in Ref. [23].

### B. Parameters, crystal template

The system studied consists of  $N = 5000$  spherical particles with diameters  $d_n$  drawn from a Bates (pseudo-Gaussian) distribution of polydispersity (defined as the ratio of the standard deviation to the mean)  $\sigma = 0$  (‘monodisperse’),  $\sigma = 0.03$  or  $\sigma = 0.06$  [24]. The mean hard core diameter  $\langle d \rangle$  sets the length unit, and the time unit is the mean time  $t_d$  taken for a free particle of diameter  $\langle d \rangle$  to diffuse a distance equal to its own diameter. The hard particle cores are surrounded by pairwise additive square wells of mean range  $\lambda = 1.15$  and depth  $u$ . The interaction range between particles  $i$  and  $j$  depends on the individual particle diameters in a scalable fashion [18, 23]:

$$V(r) = \begin{cases} \infty & \text{if } r \leq d_{ij} \\ -u & \text{if } d_{ij} < r \leq \lambda d_{ij} \\ 0 & \text{if } r > \lambda d_{ij} \end{cases} \quad (1)$$

with  $d_{ij} = (d_i + d_j)/2$ . The parent volume fraction (hereafter also referred to as ‘concentration’) is  $\phi_p = 0.34$ . In the monodisperse limit, the values of  $\phi_p$  and  $\lambda$  are such that the equilibrium state is a coexistence of crystal and gas [25]. However, by choosing  $u$  (and therefore the effective temperature  $T_{\text{eff}} = 1/u$ ) appropriately, the system’s state point can be made to lie either inside or outside the metastable gas-liquid binodal, as shown in FIG. 1 (reproduced from Ref. [25]). Given that the critical effective temperature corresponds to  $u = 1.72$ , we use a well

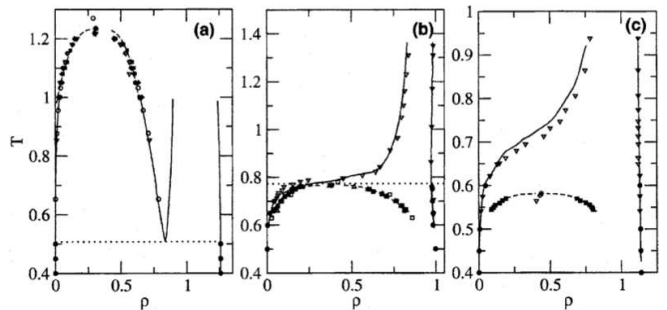


FIG. 1. Phase diagrams reproduced with permission from Ref. [25] for (a)  $\lambda = 1.5$ , (b)  $\lambda = 1.25$  and (c)  $\lambda = 1.15$  in the density-temperature plane. With our choice of units,  $T = T_{\text{eff}} \equiv 1/u$  and  $\rho = 6\phi/\pi$ . As  $\lambda$  decreases, the gas-liquid binodal becomes metastable with respect to crystal-solid separation. The relevant diagram for our system is (c).

depth of  $u = 1.82$  inside the G-L binodal and  $u = 1.54$  outside, where the energy unit is  $k_B T$ . In soft matter, one is often free to vary the interaction strength in this way, for instance by adding more or less polymer into a colloid-polymer mixture.

Since our aim is to study the process of crystal *growth*, not nucleation, we introduce crystallisation artificially by placing a  $10 \times 10$  template of immobilised particles, arranged in the (100) face of the FCC lattice, at one end of the simulation cell. The simulation cell is long in the  $x$  axis ( $L_x \approx 66$ ), and relatively short in the (periodic)  $y$  and  $z$  dimensions ( $L_y = L_z \approx 11$ ), so that the growth of the templated crystal along the  $x$  axis can be studied for a long period of time. The template’s lattice parameter is set to match the volume fraction of the equilibrium crystal [25]. Increasing the  $y$  and  $z$  dimensions of the lattice had no measurable effect on the results presented. Crystalline particles are identified by constructing bond order vectors  $\mathbf{q}_6$  from the spherical harmonics  $Y_{6m}$  [12, 26]: Particle  $i$  is flagged crystalline if  $\sum_{j=1}^{N_b(i)} \mathbf{q}_6(i) \cdot \mathbf{q}_6(j) > 8.5$ , where the sum is over the  $N_b(i)$  neighbours within  $\sqrt{1.45}r_0$  of particle  $i$ ,  $r_0$  being the average separation between particle  $i$  and its closest 6 neighbours.

After initialising the system as an amorphous fluid, the square well attraction is turned on and the template positioned, defining  $t = 0$ . An illustrative simulation snapshot shortly thereafter is shown in FIG. 2. In principle, the nucleation of independent crystals in the bulk fluid is possible, but we observe no such nucleation in the simulations presented here.

## III. THEORY

### A. Free energy landscape

Although this work is concerned with the dynamics of phase transitions, it is possible to gain a surprising

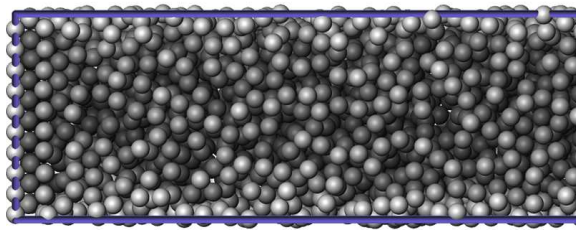


FIG. 2. Illustrative snapshot of a monodisperse system with  $u = 1.54$  at  $t \approx 100$ , showing the crystal templating method. The FCC template is positioned at  $x = 0$ , and in this case 1 or 2 further crystalline layers have so far been deposited from the bulk fluid. Approximately half the length of the simulation cell is shown. Simulation snapshots were produced using OVITO [27].

level of insight into the expected behaviour from thermodynamic considerations alone [28–30], by examining the free energy landscape of the system. To that end, we now calculate approximate fluid and crystal free energy curves for our system, in the monodisperse case, by perturbation to a hard-sphere reference system.

The free energy density  $f$  is given by:

$$f \approx f_{\text{HS}} + \frac{\rho^2}{2} \int 4\pi r^2 g_{\text{HS}}(r) U(r) dr \quad (2)$$

where  $U(r) = -u$  and  $\rho$  is the number density. The integral is over the square well range. For the hard-sphere contribution  $f_{\text{HS}}$ , we use the Carnahan-Starling free energy density [31] for the fluid, and Hall’s expression for the crystal [32]. For the hard-sphere radial distribution function  $g_{\text{HS}}(r)$ , we use the Percus-Yevick expression in the fluid [33] and that of Choi et. al. for the crystal [34].

FIG. 3 shows the resulting free energy densities plotted as functions of volume fraction for the  $u = 1.82$  case (inside the G-L binodals, for our value of  $\phi_p$ ). Allowed coexistences are given by the common tangent construction. Although quantitative agreement with the simulation data of Ref. [25] (in terms of the coexistence volume fractions of the gas and liquid phases) is relatively poor, some important qualitative features are present. The common tangent linking the minimum of the crystal branch with the gas is lower than that linking the liquid and gas – the crystal-gas coexistence therefore has a lower overall free energy and is hence the equilibrium state, while the gas-liquid coexistence is metastable. Furthermore, there is *no common tangent* between the crystal and liquid, which means that on the basis of free energy considerations, the crystal cannot locally coexist with the metastable liquid.

The lack of a crystal-liquid common tangent implies a growth scenario like that proposed for the experimental colloid-polymer mixture observations in Refs. [30, 35], in which growing crystallites are coated by a layer of colloidal gas because of their inability to coexist with the metastable liquid. This ‘boiled-egg crystal’ should

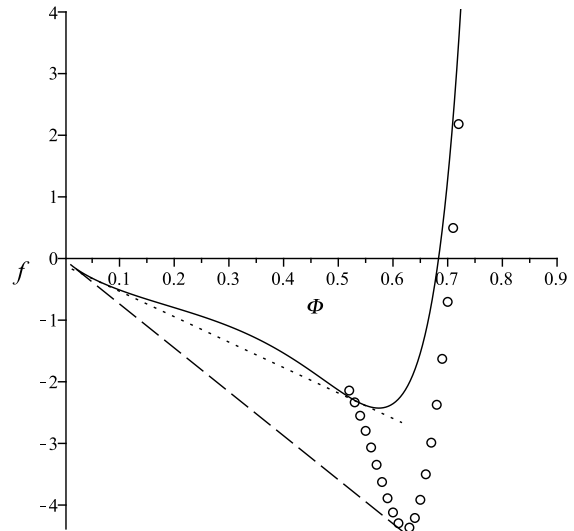


FIG. 3. Free energy density  $f$  as a function of volume fraction  $\phi$  for a monodisperse system with  $u = 1.82$  and  $\lambda = 1.15$ . The solid curve shows the fluid branch of the free energy while the circles show the crystal branch. The dotted line indicates the common tangent for metastable gas-liquid coexistence, and the dashed line shows the tangent for the equilibrium crystal-gas coexistence. There is no common tangent between the liquid and crystal phases.

deplete the surrounding bulk fluid until the required (equilibrium) crystal-gas coexistence is achieved overall. Our simulation setup allows us to model the effects of a metastable gas layer on the growth of a single crystal in a system for which we have a quantitative calculation of the corresponding free energy landscape, allowing new insight into some of the physics described in Refs. [30, 35].

## B. Split interfaces

The expected growth scenario of the ‘boiled-egg crystal’ described in Section III A is that of a ‘split interface’. That is, the crystal should form an interface with a gaseous region, which in turn forms an interface with the metastable liquid, since the crystal and metastable liquid cannot coexist on the free energy grounds discussed above. Such interfaces and a method for predicting their growth rates are described in Refs. [36, 37], wherein the example used was of a crystal-liquid-gas interface as opposed to the crystal-gas-liquid interface we expect here. We now make use of that theory to predict the evolution of the split interface that should be formed when our system is inside the G-L binodal.

As shown in FIG. 4, we assume the growth scenario to be such that the phases on each side of the interfaces are at their ‘correct’ densities according to the equilibrium phase diagram (FIG. 1), the densities  $\rho_A, \rho_B, \rho_C, \rho_D$  corresponding respectively to: the metastable liquid, the

metastable gas, the stable gas, and the stable crystal. The assumption is therefore one of local equilibrium at the interfaces.

Let  $x_1(t)$  be the position of the gas-liquid interface, and  $x_2(t)$  that of the crystal-gas interface. The respective fluxes at the interfaces,  $j_1$  and  $j_2$ , can then be related to their speeds and the densities  $\rho_i$ :

$$j_1 = \dot{x}_1(t)(\rho_A - \rho_B) \quad (3)$$

$$j_2 = \dot{x}_2(t)(\rho_D - \rho_C) \quad (4)$$

We now make the simplifying approximation that the gas region supports a uniform gradient between the densities  $\rho_B$  and  $\rho_C$ , as is the case in FIG. 4, and further that the diffusion constant therein is equal to the ideal Stokes-Einstein diffusion constant  $D_0$  due to the low density of the gas. Therefore,

$$j_1 \approx j_2 \approx D_0 \frac{\rho_B - \rho_C}{\Delta} \quad (5)$$

where  $\Delta = x_1(t) - x_2(t)$ . Substituting into Equations 3 and 4 and separating variables, with the necessary constants of integration given by the initial conditions  $x_1(t) = x_2(t) = 0$ , we find expressions for the interface positions:

$$x_1(t) = \sqrt{2D_0 \frac{\beta^2}{\gamma} t} + \sqrt{2D_0 \gamma} t \quad (6)$$

$$x_2(t) = \sqrt{2D_0 \frac{\beta^2}{\gamma} t} \quad (7)$$

where we have defined  $\beta \equiv (\rho_B - \rho_C)/(\rho_D - \rho_C)$  and  $\gamma \equiv (\rho_B - \rho_C)/(\rho_A - \rho_B) - (\rho_B - \rho_C)/(\rho_D - \rho_C)$ .

To make contact with our simulations, we read off the values of  $\rho_i$  from FIG. 1 at the appropriate effective temperature  $T_{\text{eff}} = 1/1.82 \approx 0.55$  for the systems inside the G-L binodal, and use the Stokes-Einstein diffusion constant defined by our choice of time unit,  $D_0 = 1/6$ . The resulting interface positions through time are shown in FIG. 5, and in the next section are compared with simulation data. The characteristic  $t^{1/2}$  diffusive growth is apparent, with the gas-liquid interface leading the crystal-gas interface as expected.

We note at this stage that the crystal-gas-liquid split interface scenario is very closely analogous to the crystal-liquid-gas interfaces described in Refs. [36, 37]. The only difference is that in the present work, the ‘pivot’ phase which coexists locally with both others (and therefore coats the crystal) is the gas, i.e. *is the equilibrium phase*, whereas in the aforementioned work it is the metastable, i.e. nonequilibrium liquid phase.

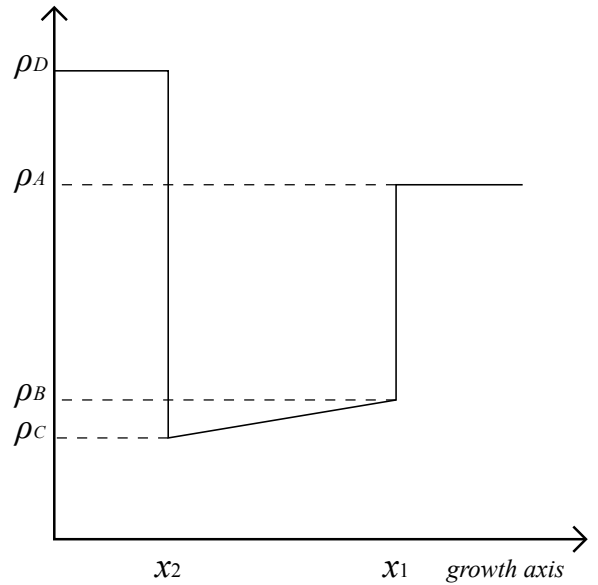


FIG. 4. Schematic density profile of the expected crystal-gas-liquid split interface inside the G-L binodal, where the crystal cannot coexist with the metastable liquid. The phases from left to right are the crystal, gas, and metastable liquid. The gradient in the gas region is drawn uniform, as is assumed in our calculations.

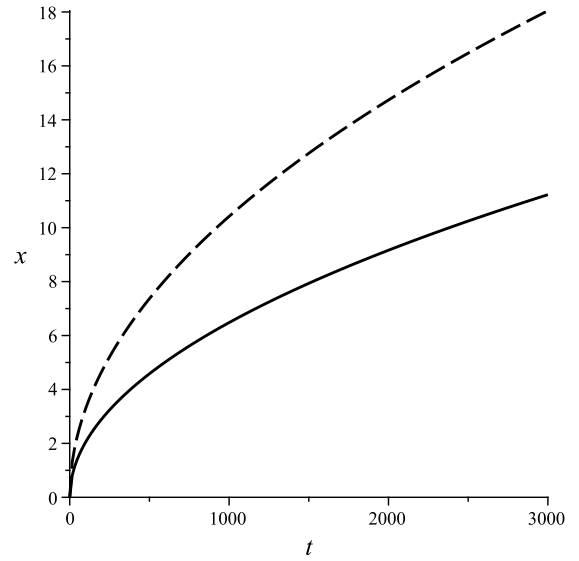


FIG. 5. The predicted evolution of the crystal-gas (solid line) and gas-liquid (dashed line) interfaces for a split crystal-gas-liquid interface when our system is inside the G-L binodal ( $u = 1.82$ ,  $\lambda = 1.15$ ).

#### IV. RESULTS AND DISCUSSION

In this section, we examine the simulation results in terms of their time-dependent concentration profiles and in terms of their crystal growth rates, elucidating and discussing the separate and combined effects of metasta-

bility and polydispersity on the growth process. Then, in Section V, we outline and briefly test a possible explanation for our findings in terms of fractionation at the crystal interface.

We present results for polydispersities of  $\sigma = 0$  (monodisperse),  $\sigma = 0.03$  and  $\sigma = 0.06$ , with square well depths of  $u = 1.82$  (inside the G-L binodal, referred to as ‘gas-mediated’) or  $u = 1.54$  (outside the G-L binodal, referred to as ‘gas-free’), giving 6 state points in total. At each state point, 6 independent initial configurations were used.

### A. Concentration profiles – monodisperse

The clearest way to visualise crystal growth over the whole simulation time is by plotting the time-dependent concentration profile. To achieve this, we plot the ‘area fraction’  $\phi_{\text{area}}$  of particles intersecting planes at a given  $x$  coordinate, corresponding to a local volume fraction in an infinitely narrow interval  $\delta x$ . Since the simulation geometry is such that the crystal interface advances along the  $x$  axis, these plots are a powerful way of observing the time evolution of concentration differences along the direction of growth while averaging over the axes perpendicular to it.

In this section, we qualitatively compare representative concentration profiles in the monodisperse and  $\sigma = 0.06$  cases. Except where noted, the phenomena described occurred similarly in all trajectories of the state point in question.

Let us consider the monodisperse case first. FIGs. 6 and 7 show example trajectories for simulations at the gas-free and gas-mediated state points respectively. In the gas-free case, the growth scenario is, as expected, relatively simple. The bulk fluid remains homogeneous, since we are above the critical  $T_{\text{eff}}$  for G-L separation. The crystal template causes the growth of a single crystalline region with an average volume fraction of  $\phi \approx 0.6$ , which is the expected equilibrium volume fraction for the crystal [25]. The crystal, being at a higher volume fraction than the bulk fluid, depletes its surroundings of particles, resulting in a concentration gradient between the local fluid and the bulk; it is this gradient which transports particles toward the crystal so that it can continue to grow.

Inside the G-L binodal (FIG. 7), the scenario is quite different. Firstly, there is clearly some G-L separation taking place in the bulk. Focusing next on the crystal template at  $x = 0$ , we can see that a region of low density gas forms in front of the crystal almost immediately, shielding it from the liquid with which it cannot locally coexist according to the free energy considerations in Section III A. This is in contrast to FIG. 6, in which the fluid immediately next to the crystal template retains its density for quite some time until the growing crystal depletes it of particles. Note also that whereas the depleted region in FIG. 6 fades smoothly into the higher density

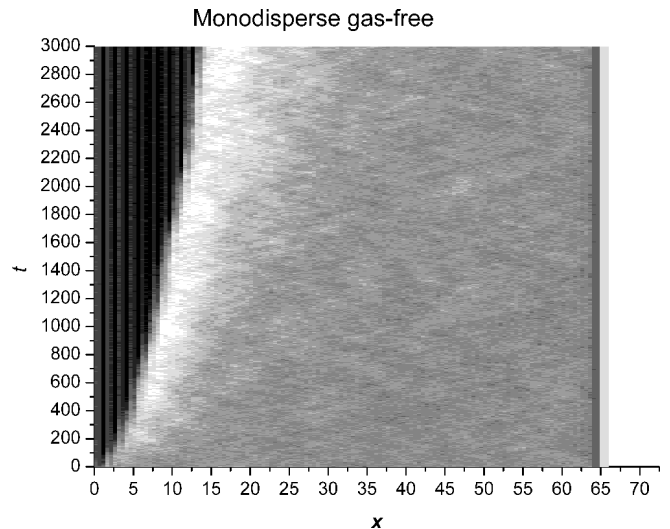


FIG. 6. Time-dependent concentration profile along the  $x$  axis for one of the monodisperse gas-free simulations. The grayscale indicates the local volume fraction, ranging from  $\phi < 0.06$  (white) to  $\phi > 0.676$  (black). As the simulation progresses, the crystal advances along the  $x$  axis, depleting the fluid in front of the interface.

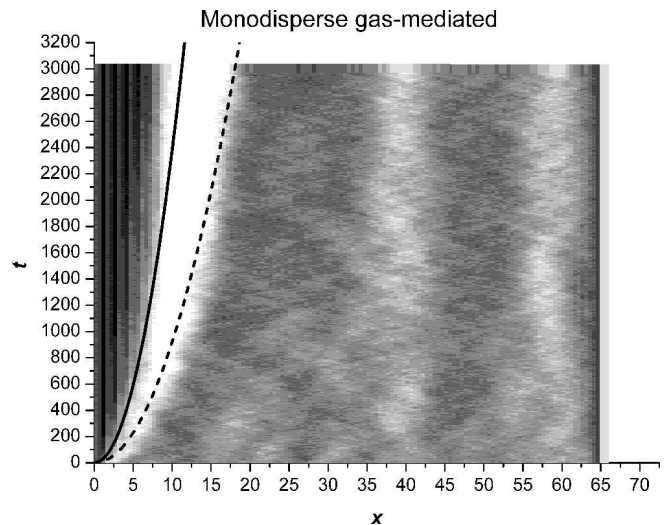


FIG. 7. As FIG. 6, for a monodisperse gas-mediated simulation. Gas-liquid separation takes place in the bulk, and the advancing crystal is coated by a distinct gas layer which advances ahead of it. The theoretical crystal-gas and gas-liquid interface curves from FIG. 5 are rotated and superimposed, showing approximate quantitative agreement with the data.

bulk fluid, the gas next to the crystal in FIG. 7 forms a substantially sharper interface with the fluid next to it, indicating a distinct phase boundary between it and the metastable liquid. The formation of this well-defined gas layer shielding the crystal is consistent with the free energy considerations above, and with the experimental observations of [30].

The speed of advancement of the crystal-gas and gas-

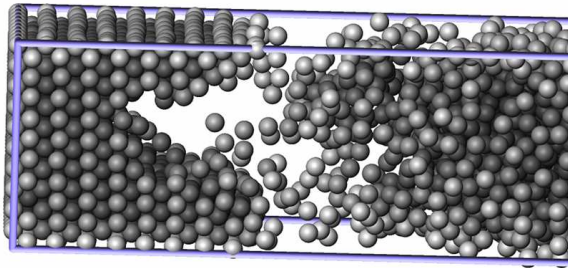


FIG. 8. Snapshot of the crystal interface for one particular monodisperse gas-mediated trajectory in which the crystal happened to exhibit dendritic growth around an impinging gas bubble. Such dendritic growth was not generally observed.

liquid interfaces is in approximate quantitative agreement with the theoretical prediction in Section IIIB (FIG. 5), which we have rotated and superimposed on FIG. 7 for comparison. This agreement is particularly satisfying given that the input densities  $\rho_i$  required for the theoretical calculation in Section IIIB were taken from the equilibrium phase diagram, so that there are no free fitting parameters. The accuracy of the prediction thus gives credence to the assumptions of local equilibration of the interfaces and of essentially ideal gas-like Stokes-Einstein diffusion in the gas region.

Finally, it is interesting to note that for some trajectories, the crystal can grow incomplete layers, as shown in FIG. 8. This is the result of dendritic growth of the crystal around an impinging gas bubble. Such growth was not found to be generally present in the other trajectories at this state point – the crystal typically formed complete layers covered by a layer of gas spanning the whole width of the simulation cell.

### B. Concentration profiles – polydisperse

We now discuss the polydisperse  $\sigma = 0.06$  case. FIG. 9 shows the gas-free scenario. On the simulated timescale, essentially no crystal growth is seen to take place, except perhaps for a slight ‘wetting’ of the template by ordered particles. As in the monodisperse case, the bulk fluid remains homogeneous, indicating that the polydispersity has not altered the location of the critical  $T_{\text{eff}}$  in such a way as might bring this state point inside the G-L binodal.

Moving to the gas-mediated case inside the binodal (FIG. 10), we can see the crystal is able to grow substantially despite the polydispersity. As in the corresponding monodisperse case (FIG. 7), the bulk fluid separates into gas and liquid regions, and a gas layer covers the crystal as it grows.

To summarise the qualitative observations in this section: the crystal template successfully induces a physically realistic growth process, in which the crystal de-

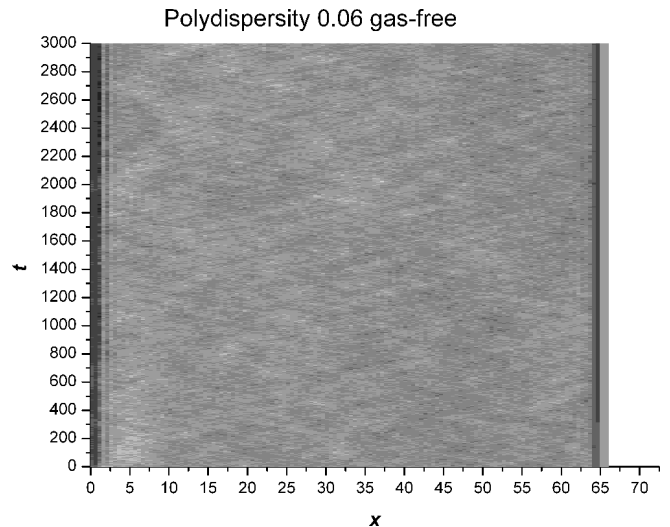


FIG. 9. As FIG. 6, for a gas-free system of polydispersity  $\sigma = 0.06$ . As in the monodisperse case, the bulk fluid remains homogeneous. However, the crystal template does not induce any growth on the timescale simulated.

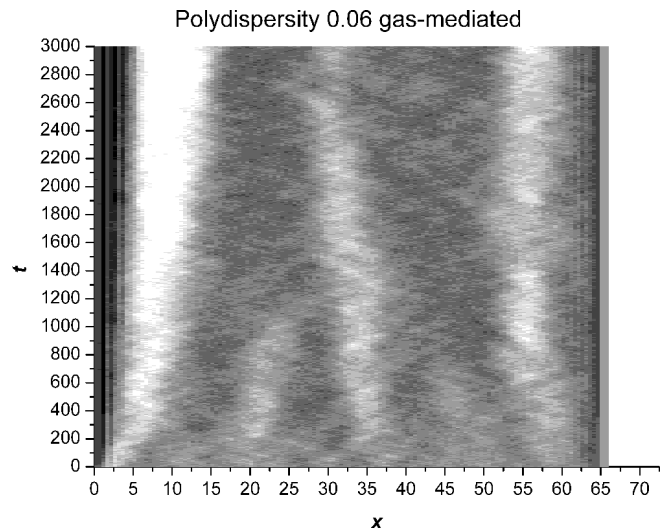


FIG. 10. As FIG. 6, for a gas-mediated system of polydispersity  $\sigma = 0.06$ . The bulk fluid shows G-L separation, and the gas layer is present in front of the crystal. In contrast to FIG. 9, the crystal is able to grow, although more slowly than in the corresponding monodisperse case (FIG. 7).

pletes its surroundings and forms ordered, high density layers. When the system is inside the G-L binodal, a gas layer forms in front of the crystal, shielding the crystal from the metastable liquid. This is exactly the scenario predicted for our system in Section III A and proposed in Refs. [30, 35]. The presence of polydispersity  $\sigma = 0.06$  substantially slowed the crystal growth overall. In the gas-free case the crystal showed barely any growth on the simulated timescale, whereas the gas-mediated case showed substantial crystal growth despite the polydispersity.



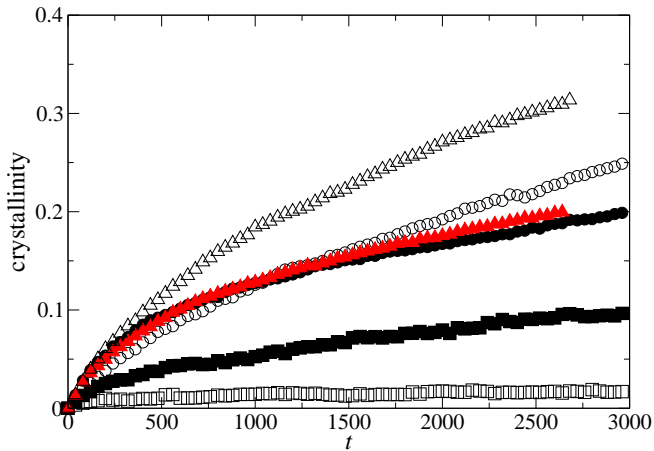


FIG. 11. (colour online) Crystallinity through time for the 6 state points studied, in each case averaged over 6 independent realisations. Filled symbols: gas-mediated; open symbols: gas-free. Triangles: monodisperse; circles:  $\sigma = 0.03$ ; squares:  $\sigma = 0.06$ . The standard errors are approximately the size of the symbols. The filled triangles (monodisperse gas-mediated) are shown in grey (red online) to distinguish them from the filled circles ( $\sigma = 0.03$  gas-mediated).

### C. Monodisperse crystal growth rate – the effect of metastability

Having summarised the qualitative features of the monodisperse and  $\sigma = 0.06$  simulations, we next quantitatively examine the effect of those features on the crystal growth rate. This is done by plotting the crystallinity (the number of particles flagged as crystalline as a proportion of the total  $N$ ) through time. FIG. 11 shows the crystal growth at each of the 6 state points studied, each averaged over the 6 independent realisations of the state point.

In the monodisperse case, the effect of metastability *alone* is apparent. The gas layer in front of the crystal significantly slows crystal growth compared to the gas-free case. The likely explanation for this is that the gas layer inhibits transport of particles into the crystal, as we now discuss.

Since the crystal exists at a higher density than the rest of the system, as soon as the immediate surroundings are depleted of particles, particles must be transported toward the crystal from the bulk in order for it to grow. This transport takes place via collective diffusion down a concentration gradient between the low concentration near the crystal and the relatively higher concentration away from the crystal. The diffusion is described by Fick's law,

$$J = -D\nabla\phi \quad (8)$$

in which  $J$  is the concentration flux,  $\phi$  is the local concentration and  $D$  is the collective diffusion coefficient. Note

that the collective diffusion coefficient, in contrast to the self diffusion coefficient, increases with  $\phi$  [38].

We now consider the phase diagram for our system, as shown in FIG. 1 (c). In the absence of the gas layer, and assuming that the interface is locally equilibrated, a long-range, relatively steep concentration gradient can exist between  $\phi \approx 0.05$  at the interface and  $\phi_p = 0.34$  in the bulk. However, inside the G-L binodal, when the crystal is covered by a distinct gas layer, the relevant concentration gradient is that which exists *across the gas layer itself* – the gas-liquid interface beyond truncates the concentration gradient. The gradient in the gas layer is between the equilibrium gas ( $\phi \approx 0.01$ ) and the slightly higher concentration *metastable* gas at  $\phi \approx 0.05$ , i.e. it is much weaker compared to the concentration gradient possible in the gas-free case.

Therefore, the low-concentration gas layer reduces the efficiency of particle transport toward the crystal because: (a) the collective diffusion coefficient  $D$  increases with concentration; (b) the gas's low concentration means it can only support a relatively weak concentration gradient in comparison to the gas-free case, in which a strong, smooth and long-range concentration gradient can exist between the interface and the homogeneous bulk. Although, on thermodynamic grounds, the driving force for crystallisation is higher inside the G-L binodal, the growth is slowed due to the gas layer's detrimental effect on particle transport to the interface.

The effect of the gas layer in the monodisperse case is comparable to that of the liquid layer in Refs. [36, 37], which was also found to inhibit crystal growth. There, as here, the crystal is coated by a phase which advances ahead of the crystal and slows down the growth of the crystal. It is interesting that this comparison holds, given that in our case the crystal is being coated by the *equilibrium* gas, whereas Refs. [36, 37] concern a crystal coated by the *nonequilibrium* liquid.

### D. Polydisperse crystal growth rates

We consider first the highest polydispersity studied here,  $\sigma = 0.06$ . As shown in FIG. 11 and in agreement with the observations in Section IV A, the gas-free state point now shows only very slight growth on the timescale simulated, whereas the gas-mediated state point shows significant crystal growth (although less than in either of the monodisperse systems). This is a *qualitative difference* compared to the monodisperse case, in which the gas layer instead strongly slows the crystal growth. That is, the presence of polydispersity qualitatively alters the effect of the metastable gas layer on crystal growth.

In the  $\sigma = 0.03$  case, the gas-mediated system is initially slightly faster, before being overtaken by the gas-free system by around  $t = 1000$ . This is suggestive of some kind of crossover phenomenon between whatever factors are dominant in the fully monodisperse and  $\sigma = 0.06$  cases.

## V. CRYSTALLISATION MECHANISM

### A. Fractionation

The results presented so far show that metastable gas-liquid separation can affect the rate of crystal growth, because it results in a gaseous layer coating the crystal as it grows. However, the qualitative nature of that effect depends strongly upon polydispersity. In the monodisperse case, the resultant gas layer impedes crystal growth by reducing the efficiency of particle transport to the crystal. With  $\sigma = 0.03$ , the slowing effect of the metastable separation is reduced, while at  $\sigma = 0.06$ , the metastable separation instead strongly enhances crystal growth. It is this effect of polydispersity on the crystal growth mechanism that we now discuss.

We propose a possible explanation in terms of a local fractionation process at the interface of the polydisperse crystal. In size polydisperse systems, it is well known that phase separation is typically associated with some degree of thermodynamically-driven fractionation in which one phase e.g. contains on average larger or smaller particles than another, changes its overall polydispersity, etc. Such fractionation has been predicted theoretically [4, 7], and observed experimentally [39] and in simulation [23]. Of course, this kind of fractionation pertains to the *equilibrium* phase composition and may not be fully achieved in real systems on accessible timescales due to kinetic factors. This is a particularly important consideration for the crystal phase, where particles are essentially stationary *once incorporated* and, thereafter, the long-range particle transport required for fractionation is facilitated only by the presence of defects. In general, phase composition is expected to relax slowly in comparison with overall density so that fractionation may lag behind phase separation somewhat [17], leading in the crystal phase to the ‘freezing-in’ of a nonequilibrium composition [18]. (Note, however, that recent work by us has shown that *some* fractionation is possible in the very early stages of gas-liquid separation [23].)

Nevertheless, we would expect that fractionation *at the interface* of the growing crystal, where particles are still mobile and may be easily exchanged with the fluid, is quite feasible. Indeed, the slowing effect of polydispersity on crystallisation is generally taken as evidence that fractionation is involved to some extent [13, 15]. We propose that such interfacial fractionation takes place not just in nucleation but during the subsequent growth of the crystal, so that it is facilitated by the low-density gas layer that forms in front of the crystal when inside the G-L binodal. In contrast to the collective diffusion discussed in Section IV C, self diffusion is hindered by particle density, so that fractionation would be frustrated outside the G-L binodal, where the fluid side of the interface is at a relatively high density compared to that in the gas-mediated case.

From the outset, we stress that a fulsome explanation of the results in the previous section requires further work

to elucidate and test other possible contributing factors, such as the influence of polydispersity on the equilibrium phase diagram. The proposals here are motivated by the dynamical nature of our simulation approach and by the intuition that the increased diffusivity of particles in the gaseous layer would help any dynamical sorting process at the crystal interface, a consideration which we expect to be a significant aspect of any full explanation of the results. In the following, we perform further analysis on the simulation data in an attempt to detect the presence of fractionation.

### B. Polydispersity of the crystal

The results we now present concern the gas-mediated and gas-free  $\sigma = 0.06$  simulations. To improve sampling in the crystal, we allowed these to run up to  $t \approx 9000$ . By this time, the crystal interface in the gas-mediated simulations reached  $x \approx 8$ , while the gas-free simulations had only grown to  $x \approx 3.5$ . We check for fractionation by measuring the mean diameter  $\langle d \rangle_{\text{cryst}}$  and polydispersity  $\sigma_{\text{cryst}}$  in the crystal. To within statistical error,  $\langle d \rangle_{\text{cryst}}$  was equal to the parental mean,  $\langle d \rangle$ .

However, changes in  $\sigma_{\text{cryst}}$  were detected. In FIG. 12, the evolution of  $\sigma_{\text{cryst}}$  in the gas-mediated and gas-free crystals is shown, as a function of time and of  $n_{\text{cryst}}$ , the mean number of particles in the crystal. In the gas-mediated case, there is a clear reduction in the polydispersity of the crystal as compared to the parental  $\sigma = 0.06$ , demonstrating that the crystal is selecting a narrower subset of the parent size distribution, eventually attaining a value of  $\sigma_{\text{cryst}} \approx 0.054$  at the end of the simulated time. This is qualitatively consistent with Fasolo and Sollich’s equilibrium calculations on hard spheres, in which even a small parental polydispersity was found to lead to reduced polydispersity in a crystal coexisting with a fluid. This measurement in itself is significant: to our knowledge, such fractionation has not previously been measured in the dynamic crystal growth of polydisperse spherical colloids (an analogous example for colloidal platelets exists in Ref. [40]), although it is proposed as an explanation of slow crystallisation in such systems [13, 15].

The data for the gas-free crystal is subject to significantly larger error, because very little crystal has actually formed, but appears to be consistent with a small reduction in polydispersity corresponding to the frustrated crystal growth. In any case, it is clear that the successful growth of a crystal involves a measurable reduction in polydispersity from the bulk fluid, indicating a fractionation process which would be enhanced by the gas layer.



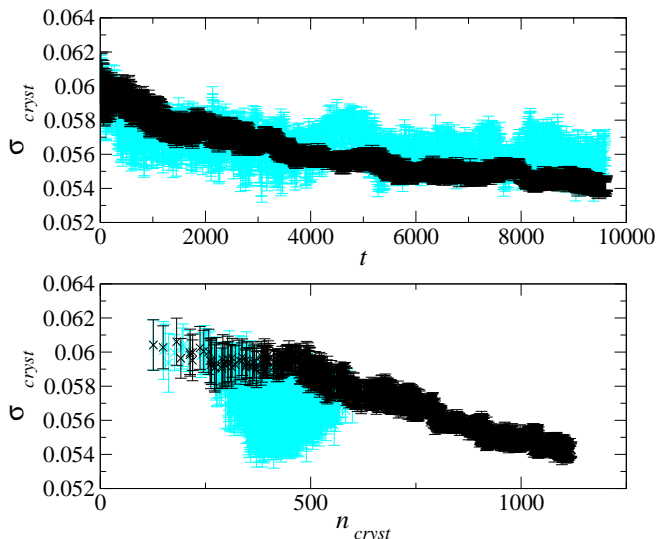


FIG. 12. (colour online) Crystal polydispersity  $\sigma_{\text{cryst}}$  as a function of  $t$  (upper pane) and  $n_{\text{cryst}}$  (lower pane) for the gas-mediated (black) and gas-free (grey, blue online, larger error bars) crystals. The error on the  $n_{\text{cryst}}$  axis is approximately 30.

### C. Summary

The results above show that the crystal phase is able to reduce its polydispersity relative to the fluid even as it is growing. We have proposed that the necessary fractionation must take place at the interface and therefore, relying on self diffusion near the interface, is enhanced by the presence of the gas layer. If true, this mechanism would explain the very slow crystallisation in the  $\sigma = 0.06$  gas-free case, where no such layer exists.

The  $\sigma = 0.03$  simulations provide an interesting intermediate case, in which the crystal growth in the gas-mediated case is initially faster before being overtaken by the gas-free case. In light of our hypothesis, this may be because the gas-free growth is relatively slower until the interfacial fluid is sufficiently depleted to allow adequate diffusion near the interface. In the gas-mediated growth, a gas layer is formed *immediately*, so that growth is initially faster. However, once the gas-free system has sufficiently depleted the interfacial fluid, the interfacial diffusion is enhanced and it now grows the fastest, the gas-mediated system lagging behind for the reasons discussed in Section IV C. In contrast, for  $\sigma = 0.06$  the gas-free growth is so slow (presumably due to the greater fractionation required) that the interfacial fluid is not depleted enough for such a crossover to happen on the simulated timescale.

We stress that the ideas outlined in this section constitute only one potential explanation of the results we observed in Section IV. Much further work will be required to determine other factors (e.g. the influence of polydispersity-induced changes to the equilibrium phase diagram), and to more rigorously test the dynamical ex-

planation outlined here (which we expect will remain an important part of any more comprehensive explanation). Nonetheless it is clear that, whatever the mechanisms, the influence of metastability on crystal growth kinetics is far from trivial, and that its role can be qualitatively switched by the presence of a very mild degree of polydispersity.

## VI. CONCLUSIONS

We have studied the kinetics of crystal growth using a model system in which a single crystal grows from an amorphous fluid. By varying the interaction strength and the polydispersity, we were able to investigate the separate and combined effects of metastable gas-liquid separation and polydispersity on the crystal growth process. Taking advantage of the pre-determined growth direction of the crystal, we have used one-dimensional concentration profiles to clearly display the phase ordering scenarios when the system is inside or outside the metastable G-L binodal. Inside the binodal, we observed the formation of a gaseous layer coating the crystal, in agreement with approximate free energy curves and with previous experimental observations of three-phase ordering. The diffusive growth of the crystal-gas-liquid ‘split interface’ was modelled theoretically, and we found approximate quantitative agreement between theoretical and simulation interface growth profiles. This agreement validated our use of two approximations in the theory, namely that the interfaces are locally equilibrated to the densities given by the phase diagram (FIG. 1) and that particle transport through the gas layer is approximately ideal gas-like due to the gas’s low density.

The dynamic influence of this gaseous layer, in the monodisperse case, was to impede growth by slowing particle transport to the crystal interface, suggesting that, while metastable G-L separation can enhance crystal *nucleation* [19, 41], it may (in the ideally monodisperse case at least) have the opposite effect on the subsequent *growth* of the crystal if the free energy landscape is such that the metastable liquid cannot coexist with the crystal, as was the case here. However, introducing a small amount of polydispersity, corresponding roughly to that found in a ‘near-monodisperse’ colloidal system, we found that the gaseous layer instead strongly *enhanced* growth.

The crystals grown show an overall reduction in polydispersity versus the parent, consistent with existing equilibrium theory and equilibrium simulations. This fractionation is often proposed as an explanation for slow crystallisation in polydisperse systems, but to our knowledge has not previously been measured in the *dynamic* crystal growth of polydisperse spherical colloids. We have postulated that this fractionation process, requiring self diffusion, is facilitated by the gas layer, perhaps explaining why this layer enhances crystal growth in the polydisperse case, rather than impeding it as in the monodisperse case.

It must be stressed that our proposed explanation requires further investigation and probably does not constitute the full story. Other factors, such as the effect of polydispersity on the equilibrium phase diagram of the system, must be considered – further work will be required to establish what effect those factors have, and to rigorously test the explanation we outlined here. Also, as with other comparable simulations, hydrodynamic interactions (HI) have been neglected; more complex and expensive simulations would be required to quantify possible effects of HI on the dynamics observed here.

We have presented a detailed dynamical study of crystal growth scenarios in the presence of metastability and polydispersity, and shown how our findings relate to the free energy landscape and equilibrium phase diagram of

the system. Whatever emerges from future work, the results demonstrate the importance of both metastability and polydispersity for soft matter phase transition kinetics and, moreover, that these two factors interact in a complex and previously unknown manner, the causes of which remain to be investigated further.

## ACKNOWLEDGMENTS

Thanks are due to N. B. Wilding, P. Bartlett and C. P. Royall for their interest and suggestions. J. J. W. was supported by an Engineering and Physical Sciences Research Council Doctoral Training Grants award.

- 
- [1] V. Prasad, D. Semwogerere, and E. R. Weeks, *J. Phys. Condens. Matter* **19**, 113102 (25pp) (2007).
  - [2] L. Onsager, *Ann. N.Y. Acad. Sci.* **51**, 627 (1949).
  - [3] R. M. L. Evans, D. J. Fairhurst, and W. C. K. Poon, *Phys. Rev. Lett.* **81**, 1326 (1998).
  - [4] R. M. L. Evans, *J. Chem. Phys.* **114**, 1915 (2001).
  - [5] P. Sollich and N. B. Wilding, *Phys. Rev. Lett.* **104**, 118302 (2010).
  - [6] P. Sollich and N. B. Wilding, *Soft Matter* **7**, 4472 (2011).
  - [7] M. Fasolo and P. Sollich, *Phys. Rev. E* **70**, 041410 (2004).
  - [8] N. B. Wilding and P. Sollich, *Europhys. Lett.* **67**, 219 (2004).
  - [9] R. Fantoni, D. Gazzillo, A. Giacometti, and P. Sollich, *J. Chem. Phys.* **125**, 164504 (2006).
  - [10] P. Bartlett and P. B. Warren, *Phys. Rev. Lett.* **82**, 1979 (1999).
  - [11] E. Zaccarelli, C. Valeriani, E. Sanz, W. C. K. Poon, M. E. Cates, and P. N. Pusey, *Phys. Rev. Lett.* **103**, 135704 (2009).
  - [12] S. R. Williams, C. P. Royall, and G. Bryant, *Phys. Rev. Lett.* **100**, 225502 (2008).
  - [13] S. Martin, G. Bryant, and W. van Megen, *Phys. Rev. E* **67**, 061405 (2003).
  - [14] S. Martin, G. Bryant, and W. van Megen, *Phys. Rev. E* **71**, 021404 (2005).
  - [15] H. J. Schöpe, G. Bryant, and W. van Megen, *J. Chem. Phys.* **127**, 084505 (2007).
  - [16] S. M. Liddle, T. Narayanan, and W. C. K. Poon, *J. Phys. Condens. Matter* **23**, 194116 (2011).
  - [17] P. B. Warren, *Phys. Chem. Chem. Phys.* **1**, 2197 (1999).
  - [18] R. M. L. Evans and C. B. Holmes, *Phys. Rev. E* **64**, 011404 (2001).
  - [19] V. J. Anderson and H. N. W. Lekkerkerker, *Nature* **416**, 811 (2002).
  - [20] N. Dixit and C. Zukoski, *J. Colloid Interface Sci* **228**, 359 (2000).
  - [21] C. Haas and J. Drenth, *Journal of Physical Chemistry B* **104**, 368 (2000).
  - [22] C. Haas and J. Drenth, *Journal of Crystal Growth* **196**, 388 (1999).
  - [23] J. J. Williamson and R. M. L. Evans, *Phys. Rev. E* **86**, 011405 (2012).
  - [24] The Bates distribution is a sum of  $n$  random numbers uniformly distributed on the unit interval – in our implementation  $n = 4$ .
  - [25] H. Liu, S. Garde, and S. Kumar, *J. Chem. Phys.* **123**, 174505 (2005).
  - [26] P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, *Faraday Discuss.* **104**, 93 (1996).
  - [27] A. Stukowski, *Modelling Simul. Mater. Sci. Eng.* **18**, 015012 (2010).
  - [28] W. C. K. Poon, F. Renth, R. M. L. Evans, D. J. Fairhurst, M. E. Cates, and P. N. Pusey, *Phys. Rev. Lett.* **83**, 1239 (1999).
  - [29] W. C. K. Poon, F. Renth, and R. M. L. Evans, *Journal of Physics: Condensed Matter* **12**, A269 (2000).
  - [30] F. Renth, W. C. K. Poon, and R. M. L. Evans, *Phys. Rev. E* **64**, 031402 (2001).
  - [31] N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).
  - [32] K. R. Hall, *J. Chem. Phys.* **57**, 2252 (1972).
  - [33] G. Stell, *Physica* **29**, 517 (1963).
  - [34] Y. Choi, T. Ree, and F. H. Ree, *J. Chem. Phys.* **95**, 7548 (1991).
  - [35] R. M. L. Evans, W. C. K. Poon, and F. Renth, *Phys. Rev. E* **64**, 031403 (2001).
  - [36] R. Evans and W. Poon, *Physical Review E*, vol. 72, Issue 5, id. 057301 **56**, 5748 (1997).
  - [37] R. M. L. Evans, W. C. K. Poon, and M. E. Cates, *EPL (Europhysics Letters)* **38**, 595 (1997).
  - [38] M. Tirado-Miranda, C. Haro-Prez, M. Quesada-Prez, J. Callejas-Fernandez, and R. Hidalgo-Ivarez, *Journal of Colloid and Interface Science* **263**, 74 (2003).
  - [39] R. M. L. Evans and D. J. Fairhurst, *Colloid. Polym. Sci.* **282**, 766 (2004).
  - [40] D. V. Byelov, M. C. D. Mourad, I. Snigireva, A. Snigirev, A. V. Petukhov, and H. N. W. Lekkerkerker, *Langmuir* **26**, 6898 (2010).
  - [41] A. Fortini, E. Sanz, and M. Dijkstra, *Phys. Rev. E* **78**, 041402 (2008).